



# High voltage and safe electrolytes based on ionic liquid and sulfone for lithium-ion batteries

Jin Xiang<sup>a,b</sup>, Feng Wu<sup>a</sup>, Renjie Chen<sup>a,\*</sup>, Li Li<sup>a</sup>, Huigen Yu<sup>b,\*\*</sup>

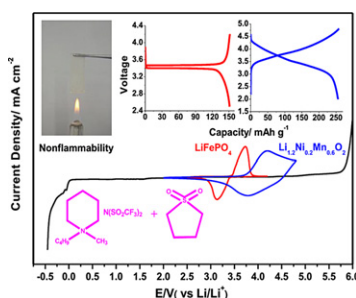
<sup>a</sup>School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing Key Laboratory of Environmental Science and Engineering, Beijing 100081, China

<sup>b</sup>Electric Drive Engineering Department, Beijing Electric Vehicle Co., Ltd, Beijing 102606, China

## HIGHLIGHTS

- ▶ Mixed electrolytes based on ionic liquid and sulfone.
- ▶ The electrolytes exhibit wide electrochemical windows and non-flammability.
- ▶ The addition of sulfone improve electrode compatibility of the electrolytes greatly.
- ▶ Lithium difluoro(oxalato)borate also has positive effects on the battery performance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Novel binary electrolytes based on ionic liquid (N-butyl-methyl piperidinium bis(trifluoro-methylsulfonyl) imide, PP14-TFSI) and sulfone (tetramethylene sulfone, TMS) have been prepared and examined for use in lithium-ion batteries. The addition of sulfone is expected to improve the lithium salts solvability, ionic conductivity and electrode compatibility of the ionic liquid greatly. More importantly, the addition of sulfone is not expected to deteriorate the peculiar properties of the ionic liquid, such as the wide electrochemical window and non-flammability. Experimental results have shown that the reversible discharge capacities of the Li/LiFePO<sub>4</sub> half-cell, which contains a 0.5 M LiTFSI/(60%) PP14-TFSI/(40%) TMS mixed electrolyte at a current density of 0.05 C and 1 C, can reach up to 160 and 150 mAh g<sup>-1</sup>, respectively, which are much higher than the discharge capacity achieved using the pure ionic liquid electrolyte under the same conditions. Furthermore, lithium difluoro(oxalato)borate (LiDFOB) has been found to have positive effects on the battery performance of the mixed electrolytes. The 0.5 M LiDFOB/(60%) PP14-TFSI/(40%) TMS mixed electrolyte exhibits better compatibility with the Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> cathode than conventional electrolytes, where an initial discharge capacity of 255 mAh g<sup>-1</sup> is obtained and a stable capacity of above 230 mAh g<sup>-1</sup> is retained after 30 cycles.

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## 1. Introduction

Lithium-ion batteries are considered to be the most promising battery technology in the field of electric vehicles (EV). However,

the current lithium-ion battery system has an inherent safety problem arising from the use of readily volatile and highly flammable organic carbonates as electrolytes [1,2]. As a result, recent efforts have been focused on finding electrolytes with a high flash point that are non-flammable [3–6]. Moreover, since novel electrode materials, such as Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub>, [7] have been developed with high operating voltages and discharge capacities, electrolytes with wide voltage windows and good electrode compatibility are also required.

\* Corresponding author. Tel.: +86 10 68451429; fax: +86 10 68918766.

\*\* Corresponding author. Tel.: +86 10 80278085 6621; fax: +86 10 80270258.

E-mail addresses: [chenrj@bit.edu.cn](mailto:chenrj@bit.edu.cn), [chenrjbit@sina.com](mailto:chenrjbit@sina.com) (R. Chen), [yuhuigen@bjev.com.cn](mailto:yuhuigen@bjev.com.cn) (H. Yu).

Ionic liquids (ILs) that consist of cations and anions have suitable properties for use as safe electrolytes because they are non-volatile and non-flammable [8–10]. In particular, ILs based on piperidium, which possess wide electrochemical windows ( $>5$  V) and a high cathodic stability against lithium metal, have attracted much attention, and their application in lithium-ion batteries has also been widely tested [11–13]. Unfortunately, the lithium-ion batteries fabricated using neat ILs as the electrolyte exhibited disappointing performances because of the low ionic conductivity and lithium corrosion problem associated with the ILs. Recent investigations have been directed to the use of IL additives to enhance the electrochemical performance of the lithium-ion batteries [14,15]. For example, considerable efforts have been focused on the use of vinylene carbonate (VC) and some other organic compounds as IL additives, the results of which have shown improvements in the electrolyte properties and the lithium-ion battery performance [9,16]. However, their low electrochemical stability on high voltage cathode materials restricts their further application [17]. Sulfone compounds possess wide electrochemical windows, high dielectric constants, and low flammability, but their use as electrolyte additives in ILs has rarely been reported. Herein, we report novel ionic liquid/sulfone mixed electrolytes based on *N*-butyl-methyl piperidinium bis(trifluoromethylsulfonyl)imide (PP<sub>14</sub>-TFSI) and tetramethylene sulfone (TMS) as high voltage and safe electrolytes for use in lithium-ion batteries. Another new additive, lithium difluoro(oxalato)borate (LiDFOB), has also been used as both a lithium salt and surface-active additive in these electrolytes.

## 2. Experimental section

The pure IL electrolyte (0.3 mol kg<sup>−1</sup> solution of LiTFSI in PP<sub>14</sub>-TFSI) was prepared by dissolving LiTFSI in PP<sub>14</sub>-TFSI (99%, Shanghai Cheng Jie Chemical Co. LTD) in an argon-filled glove box and stirring the solution at room temperature for 24 h. The ionic liquid/sulfone mixed electrolytes were obtained by adding 0.5 mol kg<sup>−1</sup> LiTFSI (or LiDFOB) and 40 wt% TMS ( $>99\%$ , Acros) in PP<sub>14</sub>-TFSI. PP<sub>14</sub>-TFSI, which was then dried in vacuo at 80 °C for 10 h before use such that it contained less than 20 ppm of water.

The assembly of Li/LiFePO<sub>4</sub> and Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> button batteries was carried out in the argon-filled glove box. The electrode consisted of an active material (LiFePO<sub>4</sub> or Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub>), a conductivity agent (acetylene black), and a polymer binder (polyvinylidene difluoride, PVDF) in a weight ratio of approximately 8:1:1.

The ionic conductivity of the electrolytes was measured using an electrochemical cell equipped with Pt electrodes at various temperatures. The cell constant was determined with a standard KCl solution (0.01 M) at 25 °C. The alternating current impedance of the samples was tested using a CHI604D electrochemical workstation (Shanghai Chenhua Company) over the frequency range of 100 kHz–1 Hz. The electrochemical window of the electrolytes was determined by conducting linear sweep voltammetry measurements on the electrochemical workstation at a scan rate of 1 mV s<sup>−1</sup> at room temperature. The electrolyte was sealed in a glass cell with a platinum wire ( $\phi = 0.1$  mm) as the working electrode and Li foil (99.9%) as the reference and counter electrodes. The alternating current impedance of the batteries was tested at the open-circuit voltage over the frequency range of 100 kHz–10<sup>−2</sup> Hz. The cell performance of the electrolytes was carried out using a Land CT2001A battery testing system using the button cells with lithium metal as the counter and reference electrodes at room temperature. The cell was charged and discharged at a constant current. For the Li/LiFePO<sub>4</sub> half-cells, the cutoff voltages were set at 4.2 and 2.5 V, and for the Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> half-cells, the cutoff voltages were set at 4.8 and 2.0 V. The flammability of the electrolytes was tested by

immersing a piece of glass fiber cloth in electrolyte, and then exposing it to a flame (spirit lamp). During the flammability test, the interval between the glass filter and the wick of the alcohol lamp was kept at 50 mm. The alcohol lamp was removed from under the glass filter after 10 s. The electrolyte was judged to be non-flammable if the electrolyte failed to ignite during the testing, or if the ignition of the electrolyte ceased when the flame was removed. Each electrolyte was tested three times.

## 3. Results and discussion

Table 1 shows the results of the flammability testing on TMS, PP<sub>14</sub>-TFSI and the PP<sub>14</sub>-TFSI/TMS mixed solvent. During the testing, the TMS ignited within 10 s and continued burning after the flame was removed, because of TMS being flammable at ambient temperature. As expected, the neat PP<sub>14</sub>-TFSI did not ignite confirming its non-flammability. It is worth noting that the PP<sub>14</sub>-TFSI/TMS mixed solvent also appeared to be non-flammable, even though it contained 40 mass% flammable organic solvent. This result can be explained by the fact that the partial pressure of the flammable gas around the test flame was decreased because of the existence of the non-flammable PP<sub>14</sub>-TFSI.

Fig. 1 compares the electrochemical stability of the neat PP<sub>14</sub>-TFSI ionic liquid and the PP<sub>14</sub>-TFSI/TMS mixed solvent by using linear sweep voltammetry measurements. The electrochemical window of neat PP<sub>14</sub>-TFSI is ca. −0.2 to 5.4 V. The anodic limiting current at 5.4 V (vs. Li<sup>+</sup>/Li) is attributed to the oxidation of the TFSI<sup>−</sup> anions, while the cathodic limiting current flow observed at −0.2 V (vs. Li<sup>+</sup>/Li) corresponds to the decomposition of the PP<sub>14</sub><sup>+</sup> cations. The addition of TMS narrows the electrochemical window of the mixed solvent slightly, but it maintains a wide electrochemical window of above 5 V because of the good electrochemical stability of TMS [18]. The results confirm the feasibility of the PP<sub>14</sub>-TFSI/TMS mixed solvent for use in high voltage cathode materials.

The ionic conductivity of 0.3 M LiTFSI/PP<sub>14</sub>-TFSI, 0.5 M LiTFSI/(60%) PP<sub>14</sub>-TFSI/(40%) TMS and 0.5 M LiDFOB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS electrolyte solutions were measured between −20 and 80 °C, and the results are shown in Fig. 2. The ionic conductivity of the neat ionic liquid electrolyte increases from 0.007 mS cm<sup>−1</sup> at −20 °C to 0.56 mS cm<sup>−1</sup> at 25 °C and reaches 5.65 mS cm<sup>−1</sup> at 80 °C. When PP<sub>14</sub>-TFSI is mixed with TMS in a 6:4 weight ratio, a significant increase in the ionic conductivity is observed even at low temperatures. The ionic conductivity of 0.5 M LiTFSI/(60%) PP<sub>14</sub>-TFSI/(40%) TMS increases from 0.14 mS cm<sup>−1</sup> at −20 °C to 2.04 mS cm<sup>−1</sup> at 25 °C and reaches 9.71 mS cm<sup>−1</sup> at 80 °C. The effect of TMS on the improvement of the bulk conductivity lies in its ability to increase the number of dissociated ions “Li<sup>+</sup>, TFSI<sup>−</sup>, or others” in the solvent mixture by increasing its dielectric constant to values presumably higher than that of PP<sub>14</sub>-TFSI. The addition of TMS is also able to enhance the mobility of those dissociated ions by decreasing the viscosity of the solvent mixture, and hence increase the bulk conductivity of the solvent mixture electrolytes, as compared with the single PP<sub>14</sub>-TFSI electrolyte. Moreover, it seems that the conductivity of the PP<sub>14</sub>-TFSI/TMS mixed electrolyte with LiTFSI is slightly higher than that of the mixed electrolyte with LiDFOB, which is probably attributed to the similarity between the anion of LiTFSI and the ionic liquid solvent.

**Table 1**  
Results of flammability testing of solvent samples.

Samples	Occurrence of ignition
TMS	3/3
PP <sub>14</sub> -TFSI	0/3
(60%) PP <sub>14</sub> -TFSI/(40%) TMS	0/3

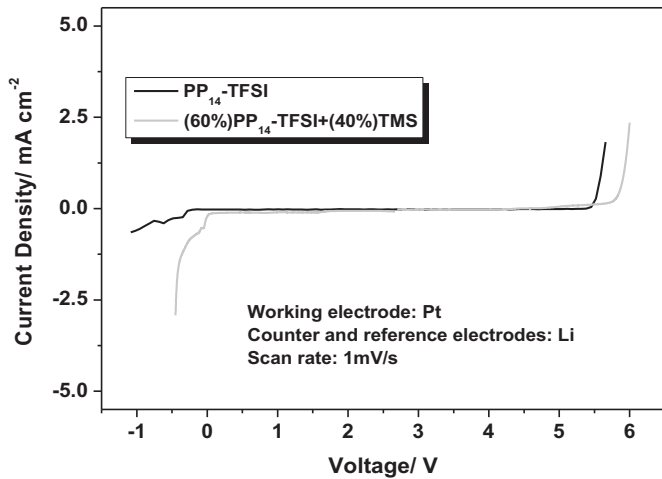


Fig. 1. Linear sweep voltammogram of PP<sub>14</sub>-TFSI and PP<sub>14</sub>-TFSI/TMS mixed solvent.

Fig. 3 displays the initial charge–discharge profiles of Li/LiFePO<sub>4</sub> cells containing neat PP<sub>14</sub>-TFSI ionic liquid electrolyte and PP<sub>14</sub>-TFSI/TMS mixed electrolytes. It can be seen that the potential difference between the charge and discharge plateaus for the electrolytes with TMS is smaller than that without TMS, which indicates that the process of lithium deposition and dissolution is smoother after the incorporation of TMS. Moreover, the initial discharge capacity and coulombic efficiency for the electrolytes with TMS are above 150 mAh g<sup>-1</sup> and nearly 100% at a constant current of ca. 0.05 C (8.5 mA g<sup>-1</sup>), respectively. In contrast, the initial discharge capacity and coulombic efficiency for the electrolyte without TMS are only around 103 mAh g<sup>-1</sup> and 82%, respectively.

Fig. 4A shows the cyclic performance of Li/LiFePO<sub>4</sub> cells containing those three kinds of electrolytes at a current density of ca. 0.05 C. The addition of TMS makes the electrolytes exhibit excellent cyclic charge–discharge capacity, almost without deterioration, which enables the electrolytes to retain 99% of their initial capacity after the 30th cycle. However, the charge–discharge capacity for the electrolyte without TMS is changed greatly and a low capacity of around 80 mAh g<sup>-1</sup> is

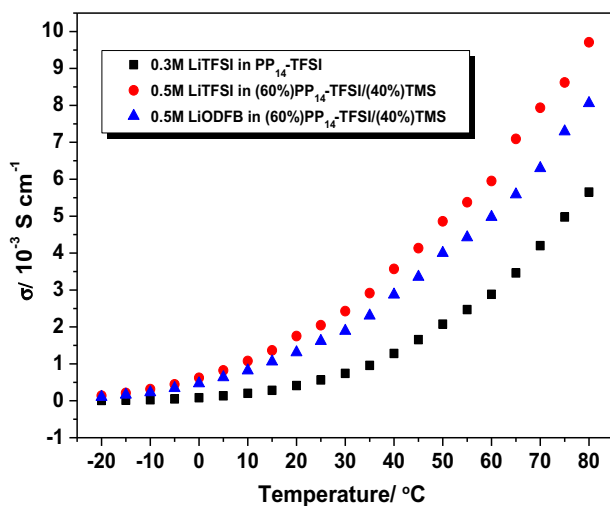


Fig. 2. Temperature dependence of the ionic conductivity for 0.3 M LiTFSI/PP<sub>14</sub>-TFSI, 0.5 M LiTFSI/(60%) PP<sub>14</sub>-TFSI/(40%) TMS and 0.5 M LiODFB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS electrolytes.

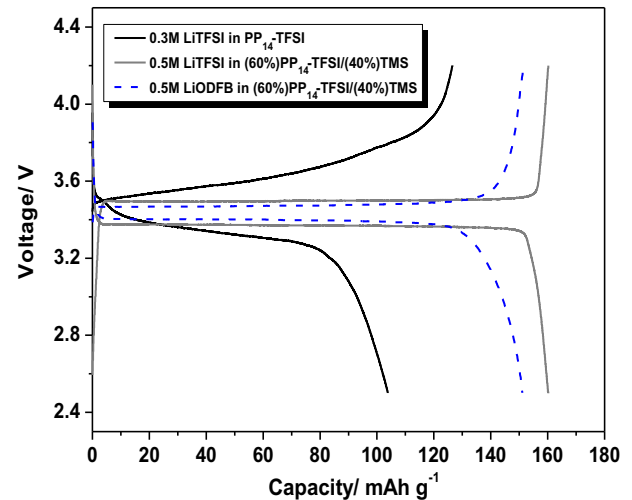


Fig. 3. Initial charge/discharge profiles of Li/LiFePO<sub>4</sub> half-cells at 0.05 C current density containing various electrolytes.

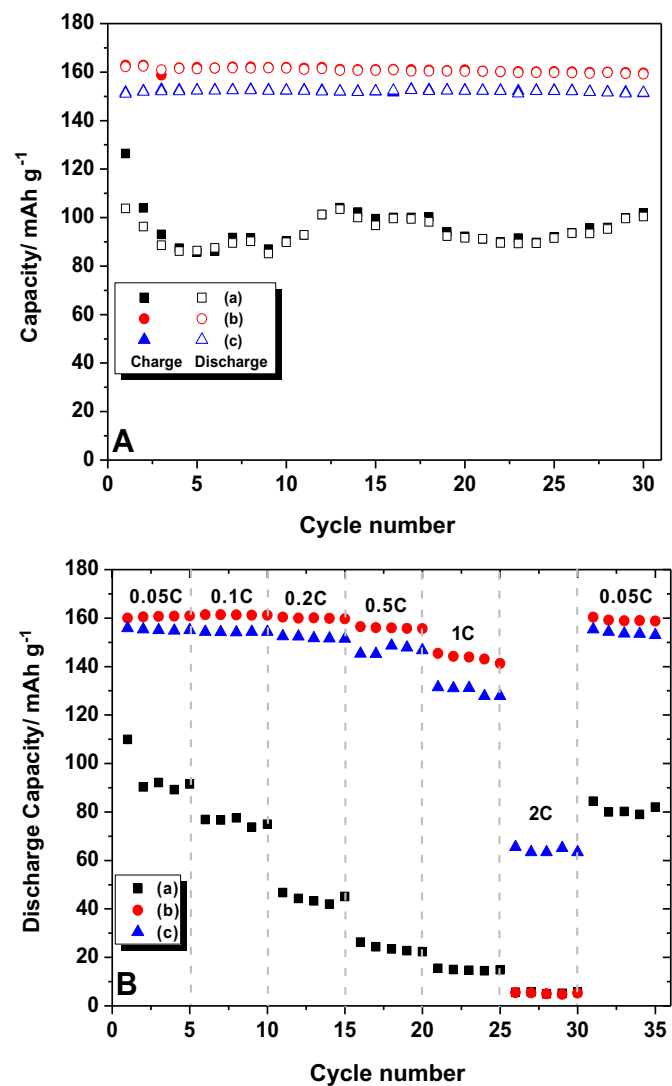


Fig. 4. (A) Charge and discharge capacities at 0.05 C current density and (B) rate performance of Li/LiFePO<sub>4</sub> half-cells containing 0.3 M LiTFSI/PP<sub>14</sub>-TFSI (a), 0.5 M LiTFSI/(60%) PP<sub>14</sub>-TFSI/(40%) TMS (b) and 0.5 M LiODFB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS (c) electrolytes.

achieved with cycling. As shown in Fig. 4B, the effect of the addition of TMS is even more significant for rate performances. The discharge capacities for the electrolytes with and without TMS at ca. 1 C ( $170 \text{ mA g}^{-1}$ ) are around 140 and  $20 \text{ mAh g}^{-1}$ , respectively. It is interesting to note that the PP<sub>14</sub>-TFSI/TMS mixed electrolyte with the LiTFSI lithium salt performs a similar discharge capacity to that of the neat ionic liquid electrolyte at ca. 2 C (nearly zero), while the mixed electrolyte with the LiDFOB lithium salt still gives a high discharge capacity of above  $60 \text{ mAh g}^{-1}$ . It is suggested that the rate performance depends not only on the Li-ion diffusion, but also on the interfacial reaction resistance of the lithium electrode [19].

To clarify the influence of the TMS and lithium salt on the interfacial properties of the electrode, AC impedance spectra of Li/LiFePO<sub>4</sub> cells containing those three kinds of electrolytes after the 1st and 30th cycles were also measured (Fig. 5). At high frequencies, the AC impedance spectra show a line with a slope of  $45^\circ$ , characteristic of porous electrodes [20,21], which then rises and falls to produce a convex curved section. This high-frequency curved section reflects the formation of a surface film on the surface of the electrode particles, which is related to the charge transfer phenomenon [22]. At low frequencies, the AC impedance spectra also show a line with a slope, which corresponds to the Warburg impedance (semi-infinite

diffusion) associated with the diffusion effects of the Li-ion on the interface between the active material particles and electrolyte [23,24]. Fig. 5A shows the equivalent circuit that has been commonly used to analyze electrochemical cell impedance spectra of battery electrodes [25,26]. In the equivalent circuit,  $R_b$  is the total resistance of electrolyte + electrode + separator,  $C_{dl}$  is the double layer capacitance,  $R_{ct}$  is the charge transfer resistance and  $W$  represents the Warburg impedance. The combination of  $R_{ct}$  and  $W$  is called the faradic impedance, which reflects the kinetics of the cell reactions. A low  $R_{ct}$  generally corresponds to a faradic reaction that has fast kinetics [27]. In fact, the  $R_{ct}$  value can be used as a kinetic parameter to analyze the corrosion rate of the electrodes [16,28], and there is a close correlation between  $R_{ct}$  and the apparent diffusivity of Li ions in the electrodes [29,30]. There are two features in Fig. 5 worthy of mention. First, the  $R_b$  value of the mixed PP<sub>14</sub>-TFSI/TMS electrolytes ( $\sim 10 \Omega$ ) is much smaller than that of the neat ionic liquid electrolyte ( $\sim 35 \Omega$ ) because of the improved lithium salt solvability and ionic conductivity after the addition of TMS. Second, those three kinds of electrolytes exhibit similar  $R_{ct}$  values after the first cycle (Fig. 5A). However, a dramatic difference appears after 30 cycles (Fig. 5B), in which the  $R_{ct}$  values of the neat ionic liquid electrolyte and mixed electrolyte with the LiTFSI lithium salt all increased rapidly up to around  $2600 \Omega$ , but only up to around  $840 \Omega$  for the mixed electrolyte

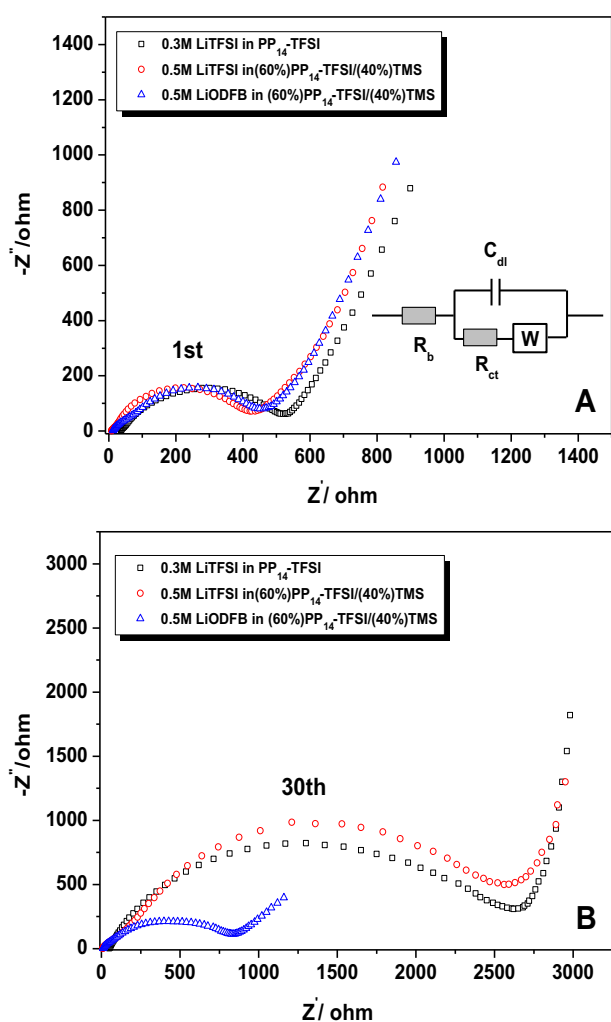


Fig. 5. AC impedance of the Li/LiFePO<sub>4</sub> half-cell using various electrolytes after (A) 1st and (B) 30th cycles. The equivalent circuit used to fit the AC impedance is shown in panel (A).

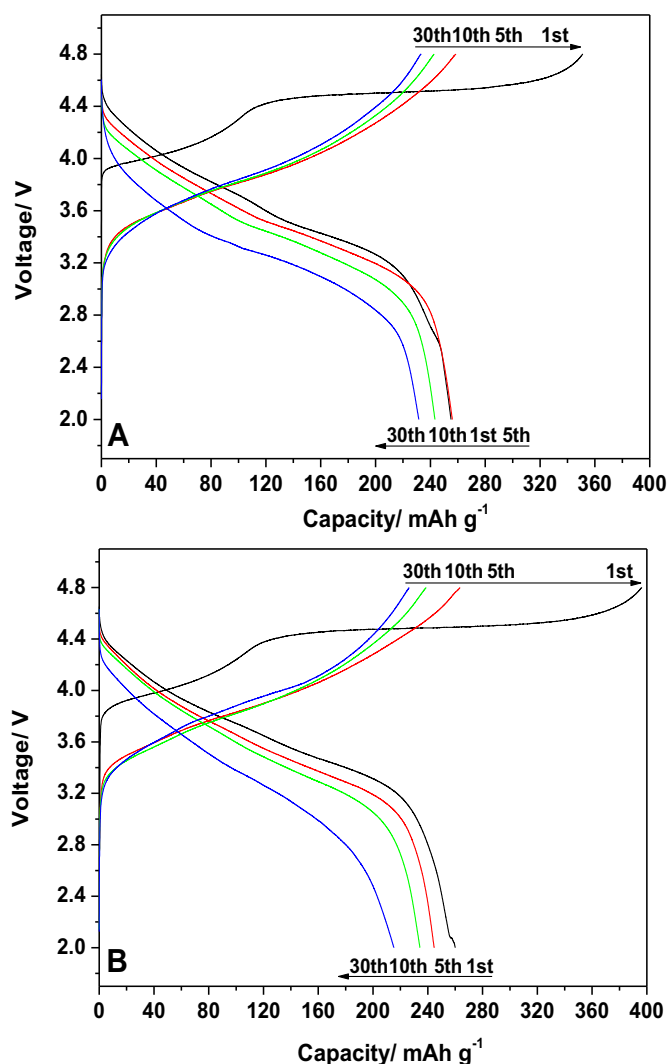


Fig. 6. Charge and discharge curves of Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> half-cells containing (A) 0.5 M LiDFOB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS and (B) 1 M LiPF<sub>6</sub>/EC/DMC (1:1).



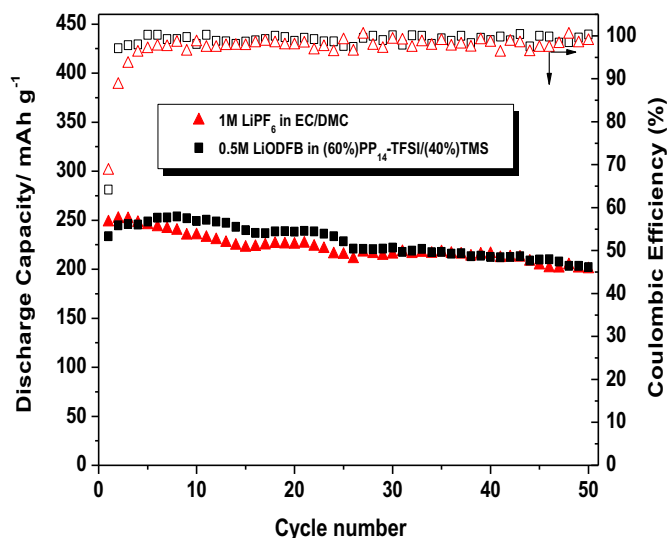


Fig. 7. Cycle performance of Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> half-cells containing 1 M LiPF<sub>6</sub>/EC/DMC (1:1) and 0.5 M LiDFOB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS at 0.1 C current density.

with the LiDFOB lithium salt. LiDFOB possesses particular properties that enable it to prevent the corrosion of the lithium electrode and show good passivation toward Al [31], which would be a reasonable explanation for its better rate performance.

We next tested the 0.5 M LiDFOB/PP<sub>14</sub>-TFSI/TMS mixed electrolyte in a Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> half-cell (Fig. 6A), where the conventional electrolyte based on 1 M LiPF<sub>6</sub>/EC/DMC was used as the reference electrolyte (Fig. 6B). The charge/discharge current density was ca. 0.05 C (12.5 mA g<sup>-1</sup>) and the cells were operated between 2.0 and 4.8 V. In general, the first charge profiles of the two electrolytes were all accompanied by an irreversible voltage plateau at ca. 4.4–4.6 V, which has been assigned to an irreversible loss of oxygen from the Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> lattice [32]. The coulombic efficiency of the cell containing the PP<sub>14</sub>-TFSI/TMS mixed electrolyte reached almost 100% after the 5th cycle, profiting from its good electrochemical stability. Nevertheless, the cell incorporating the reference electrolyte still achieved a high irreversible capacity with low coulombic efficiency (95%) even after the 30th cycle owing to the continuous decomposition of the electrolyte solvent. Furthermore, the cell containing PP<sub>14</sub>-TFSI/TMS also exhibits a higher discharge capacity after the 30th cycle (231.5 vs. 215.2 mAh g<sup>-1</sup> for the conventional electrolyte).

Fig. 7 shows the performance of the Li/Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> half-cell using a 0.5 M LiDFOB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS mixed solution and conventional solution as electrolyte for the first 50 cycles at 0.1 C (25 mA g<sup>-1</sup>). It is clear from this figure that the PP<sub>14</sub>-TFSI/TMS mixed electrolyte shows a better performance than the conventional electrolyte during the entire 50 cycles. The discharge capacities of the PP<sub>14</sub>-TFSI/TMS mixed electrolyte and the conventional electrolyte after 50 cycles are 202.2 and 200 mAh g<sup>-1</sup>, respectively. The coulombic efficiency of the cell containing the PP<sub>14</sub>-TFSI/TMS mixed electrolyte is nearly 100% after several cycles, whereas the coulombic efficiency of the cell containing the conventional electrolyte is only around 98%, even after 50 cycles. The good compatibility of the PP<sub>14</sub>-TFSI/TMS mixed electrolyte with the Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> electrode could make it a promising electrolyte for use in high-energy density lithium-ion batteries.

#### 4. Conclusion

Novel ionic liquid/sulfone mixed electrolytes based on PP<sub>14</sub>-TFSI and TMS have been prepared and examined for use in lithium-ion

batteries. The mixed electrolytes possess wide electrochemical windows and excellent compatibilities with LiFePO<sub>4</sub> and Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> electrodes. The mixed electrolytes exhibit excellent anodic stability of above 5 V, and high ionic conductivities up to 10<sup>-3</sup> S cm<sup>-1</sup> at room temperature. Lithium difluoro(oxalato)borate (LiDFOB), which consists of the half molecular moieties of lithium bis(oxalato)borate (LiBOB) and LiBF<sub>4</sub>, was used as a novel lithium salt in PP<sub>14</sub>-TFSI/TMS mixed electrolytes. It is shown that LiDFOB provides a dramatic improvement of both the capacity retention and rate performance of the cells. It was found that the 0.5 M LiDFOB/(60%) PP<sub>14</sub>-TFSI/(40%) TMS mixed electrolyte exhibits better compatibility with the Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub> electrode than a commercial electrolyte (1 M LiPF<sub>6</sub> in EC/DMC, 1:1) because of the good electrochemical stability of the PP<sub>14</sub>-TFSI/TMS mixed electrolyte. In addition, the mixed electrolytes also demonstrated good non-flammability properties. It is expected that these results will inspire researchers to perform more studies on high voltage and safe electrolytes in lithium-ion batteries for use in electric vehicles.

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#### References

- [1] Z.X. Zhang, H.Y. Zhou, L. Yang, K. Tachibana, K. Kamijima, J. Xu, *Electrochim. Acta* 53 (2008) 4833–4838.
- [2] J.B. Goodenough, Y. Kim, *Chem. Mater.* 22 (2010) 587–603.
- [3] A. Abouimrane, I. Belharouak, K. Amine, *Electrochim. Commun.* 11 (2009) 1073–1076.
- [4] S.H. Fang, Y.F. Tang, X.Y. Tai, L. Yang, K. Tachibana, K. Kamijima, *J. Power Sources* 196 (2011) 1433–1441.
- [5] G.B. Appetecchi, M. Montanino, M. Carewska, M. Moreno, F. Alessandrini, S. Passerini, *Electrochim. Acta* 56 (2011) 1300–1307.
- [6] T. Ruther, T.D. Huynh, J.H. Huang, A.F. Hollenkamp, E.A. Salter, A. Wierzbicki, K. Mattson, A. Lewis, J.H. Davis Jr., *Chem. Mater.* 22 (2010) 1038–1045.
- [7] Y.J. Zhao, C.S. Zhao, H.L. Feng, Z.Q. Sun, D.G. Xia, *Electrochim. Solid-State Lett.* 14 (2011) A1–A5.
- [8] R.J. Chen, F. Wu, B. Xu, L. Li, X.P. Qiu, S. Chen, *J. Electrochem. Soc.* 154 (2007) A703–A708.
- [9] A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagacé, A. Vijh, K. Zaghib, *J. Power Sources* 195 (2010) 845–852.
- [10] Y. Cai, Z.J. Li, H.L. Zhang, Y.J. Fang, X. Fan, J.K. Liu, *Electrochim. Acta* 55 (2010) 4728–4733.
- [11] H. Sakaebe, H. Matsumoto, *Electrochim. Commun.* 5 (2003) 594–598.
- [12] A. Lewandowski, A. Swiderska-Mocek, *J. Power Sources* 171 (2007) 938–943.
- [13] R.J. Chen, H.Q. Zhang, F. Wu, *Prog. Chem.* 23 (2011) 366–373.
- [14] B.S. Lalia, N. Yoshimoto, M. Egashira, M. Morita, *J. Power Sources* 195 (2010) 7426–7431.
- [15] H.F. Xiang, B. Yin, H. Wang, H.W. Lin, X.W. Ge, S. Xie, C.H. Chen, *Electrochim. Acta* 55 (2010) 5204–5209.
- [16] J. Jin, H.H. Li, J.P. Wei, X.K. Bian, Z. Zhou, J. Yan, *Electrochim. Commun.* 11 (2009) 1500–1503.
- [17] X.G. Sun, S. Dai, *Electrochim. Acta* 55 (2010) 4618–4626.
- [18] X.G. Sun, C.A. Angell, *Electrochim. Commun.* 11 (2009) 1418–1421.
- [19] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, *J. Power Sources* 160 (2006) 1308–1313.
- [20] A. Lasia, *J. Electroanal. Chem.* 397 (1995) 27–33.
- [21] A. Lasia, *J. Electroanal. Chem.* 428 (1997) 155–164.
- [22] H.W. Ha, N.J. Yun, K. Kim, *Electrochim. Acta* 52 (2007) 3236–3241.
- [23] Q. Cao, H.P. Zhang, G.J. Wang, Q. Xia, Y.P. Wu, H.Q. Wu, *Electrochim. Commun.* 9 (2007) 1228–1232.
- [24] F. Wu, M. Wang, Y.F. Su, S. Chen, B. Xu, *J. Power Sources* 191 (2009) 628–632.
- [25] F. Wu, G.Q. Tan, R.J. Chen, L. Li, J. Xiang, Y.L. Zheng, *Adv. Mater.* 23 (2011) 5081–5085.
- [26] S.S. Zhang, K. Xu, T.R. Jow, *Electrochim. Acta* 48 (2002) 241–246.

- [27] S.S. Zhang, K. Xu, T.R. Jow, *Electrochim. Acta* 49 (2004) 1057–1061.
- [28] H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, *J. Appl. Electrochem.* 32 (2002) 65–72.
- [29] M. Mohamedi, D. Takahashi, T. Itoh, I. Uchida, *Electrochim. Acta* 47 (2002) 3483–3489.
- [30] K. Dokko, M. Mohamedi, M. Umeda, I. Uchida, *J. Electrochem. Soc.* 150 (2003) A425–A429.
- [31] J. Li, K.Y. Xie, Y.Q. Lai, Z.A. Zhang, F.Q. Li, X. Hao, X.J. Chen, Y.X. Liu, *J. Power Sources* 195 (2010) 5344–5350.
- [32] J.M. Zheng, X.B. Wu, Y. Yang, *Electrochim. Acta* 56 (2011) 3071–3078.